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(54) Title: ION EXCHANGE RESIN (57) Abstract An ion exchange resin comprising an ion exchange material dispersed or distributed throughout a polyurethane matrix. The ion exchange material is typically a second polymer which has been chemically modified after dispersion or distribution throughout the polyurethane matrix.		

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ION EXCHANGE RESIN

5 This invention relates to ion exchange resins comprising an ion exchange material dispersed or distributed throughout a polyurethane matrix and methods of producing the same.

10 Various polymeric materials have been developed and shown to be useful in ion exchange or deionising systems for removing soluble electrolytes from an ionising solvent (typically aqueous solutions). Commercially available ion exchange resins are produced from polymers
15 such as phenol-formaldehyde, styrene-divinyl benzene, acrylonitrile, acrylates and polyamines. These polymers may subsequently be modified, for example, by halomethylation, sulphonation, phosphorylation, carboxylation, etc. Further modification of the resin so
20 produced may be achieved by a further chemical reaction to attach particular ligands to the benzene ring present in the resin or to the halomethyl, sulphonic acid, carboxylic acid, amide, amine, nitrile, or other reactive site. This further reaction enables the production of an
25 ion exchange resin with specific reactive sites thereby exhibiting greater selectivity towards particular metal ions or other anions or cations. In conventional practice, the ion exchange resins are produced in bead or granular form, the bead size generally varying from 40
30 microns to in excess of 1 mm in diameter.

Known ion exchange resins, suffer from a number of disadvantages however. To increase the available surface area of ion exchange resins which are produced in bead or
35 granular form, the polymers may be produced in a macroporous form. It has been reported that these beads can suffer from osmotic shock, poor regeneration

efficiencies, often lower sorption capacities and higher regeneration costs. In order to achieve a rapid removal of cations or anions from solution it is necessary to reduce the size of the beads to maximise the surface to
5 volume ratio.

In a typical hydrometallurgical process, the ion exchange beads may be added to a clarified lixiviant, a process solution partly clarified by removal of the
10 larger ore solids, or alternatively the ion exchange beads may be mixed with the ore solids in the form of a pulp, the granular ion exchange resin then being recovered by screening. Alternatively, the polymer may be manufactured containing a magnetic material, in which
15 case, the ion-exchange beads may be recovered by magnetic separation. It has been suggested that particularly high values for absorption are obtained if the resins are finely ground. However, fine grinding of the ion exchange resin or the use of ion exchange resin beads of
20 diameters similar to that of the ore pulp in which it is dispersed, make the resin difficult to recover by simple screening.

It has been proposed to disperse known ion exchange
25 resins into a polyurethane polymer. It has been found, however, that a chemical reaction may occur between the liquid isocyanate compound of a polyurethane system and the reactive ligand present on the surface of the ion exchange bead. The catalysts used in the production of
30 the polyurethane foam or the highly reactive isocyanate component can also react with the ligands on the ion exchange resin, destroying their ion exchange properties. Such a reaction may become one of a number of competing chemical reactions which occur during the production of a
35 cured polyurethane resin from liquid components. If the ion exchange resin has an active hydrogen ion, the acidic property will be neutralized by the alkaline catalyst,

destroying both the urethane foam reaction and the ion exchange property of the resin. It has also been proposed to add finely ground ion exchange beads to a flexible polyurethane foam prior to foaming. It has been
5 reported, however, that the presence of the ion exchange bead in the foaming system adversely affected the foaming reaction and the physical properties of the cured foam.

It is an object of the present invention to produce
10 an ion exchange resin which overcomes or alleviates one or more of the difficulties associated with the prior art.

According to the present invention there is provided
15 an ion exchange resin comprising an ion exchange material dispersed or distributed throughout a polyurethane matrix.

The term "ion exchange resin" when used herein
20 includes any polymeric material capable of removing anions and/or cations from solution by sorption irrespective of the mechanism.

The term "dispersed or distributed" when used herein
25 includes a dispersion of discrete particles as well as networks of polymers which are intimately mixed throughout or incorporated within the polyurethane matrix such in interpenetrating polymer systems.

30 The ion exchange resin comprises a urethane polymer as a matrix or continuous phase. The ion exchange material typically takes the form of a modified second polymer dispersed or distributed throughout the polyurethane matrix. The second polymer or dispersed or
35 distributed phase polymer is chemically modified after it is dispersed or distributed throughout the polyurethane matrix, by methods which will subsequently be discussed,

to obtain the required ion exchange properties.

Polyurethane formulation and manufacture in many forms is well known. Polyurethane resins can be produced
5 in a range of shapes and forms for example beads including microcellular beads and expanded beads, foams including elastomeric foams, films, fibres and membranes.

Therefore the ion exchange resin of the present
10 invention can be produced in a form best suited to a particular application or process. For example, larger particles of open cell polyurethane having a suitable ion exchange material dispersed therein, when incorporated into a resin-in-pulp based metals recovery process can
15 easily be removed from the pulp by screening. Standard ion exchange resins are difficult to separate from pulps by simple screening procedures. Polyurethanes particularly those based on polyether polyols have the further advantage that they exhibit excellent resistance
20 to both acidic and alkaline solutions, have good abrasion resistance and good flexibility over a wide range of temperatures and may be formulated to obtain a controlled degree of hydrophilicity.

25 The dispersed or distributed phase polymer typically may be a polymer formed from monomers of styrene, acrylonitrile, vinyl chloride, vinylidene chloride, divinyl benzene, butadiene, epichlorohydrin, caprolactone, thiodiglycol, thiodianiline, diallylamine,
30 methylacrylonitrile, hydrazides, dicyclopentadiene, vinyl butyral, succinic anhydride, allyl halides, allyl malonic acid, acryloyl chloride, polyacetal, vinyl alcohol, aminosalicyclic acid, dimethylolpropionic acid, α -methyl styrene, p-methyl styrene, acrylates such as
35 methylmethacrylate, acrylamide, methylacrylamide, acrylic acid, hydroxyethyl acrylate, hydroxypropyl acrylate, glycidyl methacrylate, ethylene dimethacrylate,

- methylacrylic acid, hydroxyethyl methacrylate, ethylene glycol dimethacrylate, ethyl acrylate, acrylimido salicylic acid, acrylimido diacetic acid, acrylimido malonic acid, acrylimido phthalic acid, acrylimido glycolic acid, or combinations of these monomers or chemical modifications of these monomers but is not limited to these monomers. Such chemical modification may be, for example, chlorination, hydroxylation, sulphonation, nitration, amination and the like.
- 10 Examples are hydroxy styrenes, vinylbenzyl chloride, hydroxyethyl styrene, α -methyl styrene, p-methyl styrene, dihydroxyethyl styrene, styrene sulphonic acid, acetoxy styrene.
- 15 Typical polymers which may form the dispersed phase include polystyrene, styrene-divinyl benzene, styrene-acrylonitrile, styrene-acrylonitrile-methylmethacrylate, acrylonitrile-methylmethacrylate, polyacrylonitrile, polyacrylates, acrylic or methacrylic esters,
- 20 acrylonitrile-unsaturated dicarboxylic acid-styrene, vinylidene chloride-acrylonitrile, epoxy(glycidyl methacrylate)-acrylonitrile, poly p-methylstyrene, polyureas, aniline-phenol-formaldehyde, phenol-formaldehyde, styrene-butadiene, styrene-acrylonitrile-
- 25 butadiene, acrylonitrile-polyethylene glycol, polyamides, polyacrylamides, polyimidazoles, allylglycidyl ether adducts of diamines, ethylene and propylene carbonate adducts of diamines, polybutadiene-acrylates, polydiallylamine, epoxy adducts, polycaprolactone,
- 30 caprolactone-acrylates, polydicyclopentadiene, styrene-methacrylonitrile, methacrylonitrile-divinylbenzene, polyvinyl chloride, glycidyl methacrylate-ethylene dimethacrylate, acrylonitrile-methylacrylic acid, polyvinyl alcohol-acrylonitrile, methyl methacrylate-
- 35 hydroxyethyl acrylate, hydroxyethyl methacrylate-oligo(ethylene glycol)dimethacrylate, hydroxystyrene-methylmethacrylate, polyethyl acrylate-polystyrene,

crosslinked butadiene, polystyrene-polyethyleneimine, polystyrene-arsenazo, epoxy-polystyrene, epoxy-diaza crown ethers, polyacetal, cresol sulphonic acid-phenol-formaldehyde, anthraquinone-formaldehyde, acryloyl chloride-iminodiacetic acid, acryloyl chloride-aminosalicylic acid, acryloyl chloride-methyl nitrophenol-triethylamine, methyl nitrophenol-acetic anhydride-acrylic acid, hydroxy acetophenone-substituted benzoic acid-formaldehyde, or, other like polymers or combination of polymers.

The chemical modification may also modify the polyurethane matrix. For example ligands may be attached to the urea groups, reactive methyl groups, or to the aromatic ring of the isocyanate component of the polyurethane matrix if an aromatic isocyanate is used in the production of the polyurethane resin. Additionally, reactive sites may be incorporated into the polyurethane by modifying an isocyanate with a material containing reactive sites (such as a dihydroxy compound) to form a prepolymer and further reacting the prepolymer with additional materials to produce the desired polyurethane.

The dispersed or distributed phase polymer is chemically modified by methods known in the art after it is dispersed or distributed throughout the polyurethane matrix. For example, by chloromethylation, sulphonation, carboxylation, amination, phosphorylation, thioureation, diazotization, amidoximation, oximation, etc. or other processes to attach specific ligands to the dispersed phase polymer to provide the ion exchange resin with the desired ion exchange properties. The chemical modification of the dispersed phase polymer may take place in one or more steps. For example, the dispersed phase polymer may be modified by halomethylation, sulphonation, amination, carboxylation or other applicable modification. A further modification of the

ion exchange resin so produced, may be achieved by chemical reaction to attach particular ligands to the halomethyl, sulphonic acid, amine, amide, carboxylic acid or other site. This further reaction may be, for example, amination, phosphorylation, thioureation, diazotization etc.

The desired chemical reaction generally occurs by an appropriate choice of the dispersed phase polymer and chemical conditions suitable to attach the required ligand. For example, phosphonate esters, phosphinic acid ligands etc. may be incorporated by chloromethylating a polyurethane interpenetrating polymer system containing polystyrene styrene-divinyl benzene and then further reacting the chloromethylated polystyrene with phosphorus trichloride, phosphorus oxychloride, etc. in the presence of a Friedel-Crafts catalyst such as aluminium trichloride. This reaction is normally conducted at temperatures ranging from 0°C to 75°C. Or, the phosphonate esters, phosphinic acid ligands etc. may be incorporated by reacting the benzene rings present in the polyurethane and/or which have been provided by the interpenetration of the polyurethane with polystyrene-divinyl benzene with phosphorus trichloride, phosphorus oxychloride, etc. in the presence of a Friedel-Crafts catalyst such as aluminium trichloride. This reaction is normally conducted at temperatures ranging from 0°C to 75°C. Alternatively, a polyurethane interpenetrating polymer system containing p-methylstyrene may be chloromethylated using sodium hypochlorite and a catalyst such as benzyltriethylammonium chloride at room temperature under an argon atmosphere. The chloromethylated groups may then be further reacted to add ligands such as sulphonic, carboxylic, phosphoric acid etc. To assist the reaction, the polyurethane interpenetrating polymer system may be swollen in a solvent such as toluene. Other reactions can be

similarly conducted. This technology is not limited in its scope to the examples given.

According to a further embodiment of the present invention there is provided a method of producing an ion exchange resin comprising:

providing a polyurethane matrix and subsequently having a second polymer dispersed or distributed therein by interpenetrating the polyurethane polymer with polymerisable monomers and subsequently curing them; and chemically modifying said second polymer to obtain desired ion exchange properties.

The chemical modification may also modify the polyurethane matrix. For example ligands may be attached to the aromatic ring of the isocyanate component of the polyurethane matrix if an aromatic isocyanate is used in the production of the polyurethane resin.

The ion exchange resins of the present invention may be produced from known polyurethane interpenetrating polymer systems. Therefore, according to a further embodiment of the present invention there is provided a method of producing an ion exchange resin comprising:

providing a polyurethane interpenetrating polymer system which comprises a polyurethane polymer having a second polymer dispersed or distributed therein; and chemically modifying said second polymer to obtain the desired ion exchange properties.

Polyurethane interpenetrating polymer systems can be formed by sequential polymerisation, latex blending and simultaneous blending. They are typically intimate mixtures of two or more cross-linked polymer networks held together by permanent topological entanglements (catenation). Typically polyurethane interpenetrating polymer systems are produced from two or more different

monomers or low molecular weight prepolymers and cross-linking agents of the component polymers. These are then polymerised/cross-linked simultaneously via non-interfering reaction mechanisms. By this procedure,
5 elastomeric polyurethane polymers are typically produced as a continuous phase containing micron and submicron sized beads of a second and different polymer as a dispersed phase. The polyurethane phase may be linear or cross-linked.

10

Interpenetrating polyurethane polymers can be produced in which the dispersed phase may be for example polystyrene, poly(methyl methacrylate), acrylic acid-styrene copolymer, acrylic copolymer or vinyl chloride
15 copolymer, or other monomers or copolymers. A polyurethane is impregnated with one or more monomers in the presence of suitable catalysts and the matrix so obtained is subsequently cured.

20

The above polyurethane interpenetrating polymer systems may be chemically modified as described above to obtain desired ion exchange properties.

According to yet another embodiment of the present
25 invention there is provided a method of producing an ion exchange resin comprising:

providing a polyol having a second polymer dispersed therein;

30 reacting said polyol with a diisocyanate or a blend of diisocyanates to produce a polyurethane having said second polymer dispersed therein; and

chemically modifying said second polymer to obtain desired ion exchange properties.

35

Polymer/copolymer polyols are known in which a monomer, or a blend of monomers has been polymerised in the polyol to produce a polyol having a second polymer

dispersed therein. For example a polyol is known which is based on glycerine which has been reacted with propylene oxide or a combination of ethylene oxide and propylene oxide to produce a polyether triol with a molecular weight generally in excess of 3000. Styrene and acrylonitrile monomers are then polymerised within this polymer to produce a polymer/copolymer polyol. Other polyols used in the production of elastomeric polyurethane may also be used as may other monomer combinations. This polymerisation process generally produces microscopic beads dispersed throughout the polyol raw material.

The polyurethane is produced by the reaction of the above polymer/copolymer polyol with a diisocyanate or a blend of diisocyanates. The polymer/copolymer polyol may be blended with other hydroxyl-containing polyols. The reaction may occur in the presence of catalysts, surfactants, plasticizers, fire retardants, fillers, etc. and water if a foamed material is desired. A polyurethane, is formed, having a second polymer dispersed or distributed throughout the continuous phase. The second polymer is capable of being chemically modified.

Typical polymers which may form the dispersed phase are as described above. The chemical modification to produce the desired ion exchange properties are as described above.

In still another embodiment of the present invention, there is provided a method of producing an ion exchange resin comprising:

providing a polyurethane containing a resin having ion exchange properties dispersed or distributed therein; and chemically modifying said resin to modify the ion

- 11 -

exchange properties.

Modification of the ion exchange process may be further achieved by the incorporation of melamine, 5 melamine-formaldehyde or solvent extractants containing phosphorus, or nitrogen or sulphur or any combination of these into the interpenetrated polymer. In the case of melamine this may be achieved by the incorporation of melamine in particulate form, or sufficiently reacted 10 with formaldehyde, paraformaldehyde, etc. under alkaline conditions to render the dispersed phase melamine-formaldehyde polymer water insoluble. Incorporation of melamine or melamine formaldehyde and phosphorus-containing additives are used in foam production to 15 provide fire retardancy to the cured polymer. The incorporation of these additives or other phosphorus based additives such as tributyl phosphate or nitrogen containing additives such as trioctyl amine into the ion exchange resin of the present invention may act in a 20 synergistic fashion with other ion exchange ligands.

The incorporation of melamine could also provide additional sites for chemical modification.

25 Additionally, other extractants such as water insoluble solvent extractants may be incorporated into the polyurethane prior to, or subsequent to, curing to further modify the ion exchange or chelating properties of the ion exchange resin of the present invention.

30 Polyurethanes with controlled levels of urea groups present can also be obtained. The urea groups may be reacted such as with carbon disulfide or other similar sulphur-containing reagents (eg. H_2S) to further modify 35 the properties of the ion exchange resins.

If it is considered desirable that the polyurethane

- 12 -

matrix exhibit hydrophilic properties, this may be accomplished by known procedures. For instance, if part or all of the propylene oxide is replaced by ethylene oxide during production of the polyol raw material, the polyol so produced will make the polyurethane more hydrophilic. The position of the ethylene oxide units can further modify the metal ion sorption properties of the polyurethane. The combination of the position and percentage of the ethylene oxide units when combined with particular catalyst systems can improve both the chemical resistance and metal sorption properties of the polyurethane, as illustrated in Example 2. The inclusion of polyethylene glycol in the polyurethane formulation during manufacture will also enhance the hydrophilic properties of the final product.

A further advantage of the ion exchange resins of the present invention is that the majority of the reactive ligands will be located close to or at the surface of the dispersed phase polymer thereby enabling favourable ion exchange kinetics to be achieved.

The polymeric ion exchange resins of the present invention may find application in waste water treatment and in the recovery of metal values from solution in hydrometallurgical processes. They offer a number of significant advantages over existing ion exchange beads, particularly the ease of producing the polyurethane in a wide variety of forms and shapes, which both enhances their subsequent recovery or removal from process streams and extends the scope of industrial application. The combination of desirable physical and chemical properties, and in particular, their excellent abrasion resistance and good flexibility improves their mechanical performance; the micron or submicron sized ion exchange particles contained in the polyurethane matrix or the ligands attached to the polyurethane matrix provide a

- 13 -

rapid uptake of ions from solution.

Therefore according to a further embodiment of the present invention there is provided a method for
5 recovering soluble electrolytes in a hydrometallurgical process including:

contacting an ion exchange resin as hereinbefore described with a solution containing a suspension of ore solids; and

10 recovering the ion exchange resin.

Ions such as gold, zinc, copper, chromium, palladium, platinum, silver, cobalt, mercury, arsenic, molybdenum and mixtures thereof may be recovered. The
15 person skilled in the art will of course recognise that many other ions may be recovered using the process described above.

The ion exchange resin may be in the form of
20 granules which may be recovered by screening or the ion exchange resin may contain a magnetic material and the ion exchange resin may be recovered by magnetic separation.

25 The present invention also provides a method of recovering soluble electrolytes from waste water comprising:

contacting an ion exchange resin as described above with said waste water; and

30 recovering the electrolytes from the ion exchange resin.

The waste water may be for example an industrial effluent or sewage effluent and any desired metal ions
35 may be recovered. The process of the present invention may therefore be used to treat effluents to remove toxic metals to meet the requirements of environmental

- 14 -

regulations. The metal ions and/or the effluent may be subsequently recycled.

The present invention will now be more fully described with reference to the accompanying examples. It should be understood, however, that the descriptions following are illustrative only and should not be taken in any way as a restriction on the generality of the invention described above.

10

EXAMPLE 1

EXAMPLES BASED ON INCORPORATION OF LIGANDS DIRECTLY ON TO THE POLYURETHANE POLYMER

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A polyurethane foam was produced by blending a 3800 MW polyol with the desired quantity of water to achieve the required degree of expansion, together with silicone surfactants, and catalysts, then reacting this mixture with the requisite quantity of toluene diisocyanate to produce a polyurethane foam. The polyol selected was based on glycerine and contained approximately 13% of poly(ethylene oxide) (as measured by NMR) in a block of ethylene oxide units, the remainder being poly(propylene oxide) units.

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EXAMPLE 1A

AMINATION

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1 gram of the polyurethane was reacted with 0.4 grams of dimethylamino-1-chloroethane together with 80 ml 1 M sodium hydroxide. The reaction was conducted at 80°C for 4 hours. The polyurethane was washed in water until neutral and vacuum dried at 60°C.

35

0.1 gram of the treated polyurethane foam was

- 15 -

contacted for 2 hours with 20 ml of a 50 ppm chromium(VI) solution at a pH value of 2.0. The treated polyurethane sorbed 60% of chromium(VI), whereas the untreated polyurethane only sorbed 11% of chromium(VI) under the same conditions.

EXAMPLE 1B

PHOSPHORYLATION

10

1 gram of polyurethane was placed in 70 ml of toluene then reacted at room temperature for four hours with 2.5 ml of phosphorus oxychloride in 10 ml of pyridine. The foam was then washed in water, 1M hydrochloric acid, and again in water until neutral, then vacuum dried at 60°C.

0.1 gram of the treated polyurethane was contacted with 20 ml of a solution containing 50 ppm copper(II) plus 50 ppm of zinc(II) plus 50 ppm of cobalt(II) for 2 hours. The treated polyurethane removed 87% of the copper(II), 66% of the zinc(II) and 56% of the cobalt(II) from an aqueous solution at a pH of 5.0, whereas the untreated foam did not indicate any observable removal of metal ions under the same conditions.

EXAMPLE 1C

CARBOXYLATION

30

1 gram of the polyurethane was treated with 1 gram of monochloroacetic acid in a 1M solution of sodium hydroxide at 80°C for 15 hours. The polyurethane was washed in water until neutral and vacuum dried at 60°C.

35

0.1 gram of the treated polyurethane foam was contacted with 20 ml of the solution containing 50 ppm

- 16 -

copper(II) plus 50 ppm of zinc(II) plus 50 ppm of cobalt(II) for 2 hours. The treated polyurethane selectively removed 13% of copper(II) from the mixed solution at a pH value of 5.0, whereas the untreated foam failed to remove copper from solution.

EXAMPLE 1D

CHLORINATION

10

1 gram of the polyurethane foam was placed in 80 ml of 1,2 dichloroethane and then treated at 60°C for 16 hours with 5 ml of 125 g/l sodium hypochlorite solution in the presence of benzyl trimethylammonium chloride as a catalyst. The foam was washed in water until neutral and dried in an oven. Chemical reaction was confirmed by NMR spectroscopy which indicated a loss in the N-H signal. The polyurethane exhibited improved chemical and solvent resistance.

20

EXAMPLE 2

EFFECT OF FORMULATION AND CATALYST ON THE CHEMICAL RESISTANCE AND SORPTION PROPERTIES OF A POLYURETHANE

25

Polyurethane foams were produced from a blend of a 5000 MW polyol containing a high content of poly(ethylene oxide) units with a 4800 MW poly(ethylene oxide) capped polyol under different catalyst regimes. The polyols were both based on glycerine, one containing approximately 75% of poly(ethylene oxide) units and the other, 15% of poly(ethylene oxide) units as a capping (ethylene oxide content was determined by NMR), thus many of the terminal units consist of primary hydroxyls thus providing the polyol with self-catalysing properties. The formulations contained similar levels of water, silicone surfactant, and toluene diisocyanate. One foam

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- 17 -

was produced with stannous octoate as a catalyst, the other foam did not contain this catalyst.

The polyurethane containing the stannous octoate catalyst was observed to have a significantly improved chemical resistance and was used in the following examples:

EXAMPLE 2A

10

The polyurethane described above and containing stannous octoate as a catalyst was observed to have a significant improvement in chemical and solvent resistance to the polyurethane produced without this catalyst. For example, it resisted attack by dimethyl sulphoxide and by methyl sulphonic acid, whereas the other polyurethane was rapidly swollen by these solvents and dissolved in them. Mössbauer spectroscopy indicated that potassium ferricyanide when loaded on to this polyurethane produced a paramagnetic relaxation spectrum; whereas, this relaxation was not observed with the polyurethane produced without the stannous octoate catalyst.

25

EXAMPLE 2B

THIOAMIDATION

1 gram of the above polyurethane containing the stannous octoate catalyst was reacted at 50°C for 2 hours with 10 ml of formaldehyde in 70 ml of water then further treated with 4 ml of carbon disulphide in 80 ml of water at 50°C for 15 hours. The polyurethane was thoroughly washed in water then soaked for 30 minutes in 1M NaOH, then again washed with water until neutral and vacuum dried at 60°C.

- 18 -

0.1 gram of the treated polyurethane was contacted with 20 ml of a solution containing 50 ppm copper(II) plus 50 ppm of zinc(II) plus 50 ppm of cobalt(II) for 2 hours. The treated polyurethane selectively removed 8% of the copper(II) from an aqueous solution at a pH of 5.0, whereas the untreated foam did not indicate any observable removal of metal ions under the same conditions.

10

EXAMPLE 3EXAMPLES BASED ON INCORPORATION OF INTERPENETRATING
POLYMER INTO POLYOL PRIOR TO PRODUCTION OF POLYURETHANE

15

The following examples are based on a polyol which contains a dispersion of 40% of a polystyrene-acrylonitrile copolymer in a 4800 MW glycerine based poly(ethylene oxide), poly(propylene oxide) polyol. To this polyol was added water, silicone surfactants, and catalysts and the mixture was then reacted with the requisite quantity of toluene diisocyanate to produce an expanded copolymer-containing polyurethane foam.

20

EXAMPLE 3A

25

AMINATION

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1 gram of the copolymer-containing polyurethane foam was reacted at 90°C for six hours with 0.1 g diethylenetriamine in 80 ml of toluene and in the presence of rubeanic acid as a catalyst. The polyurethane was washed in water until neutral and vacuum dried at 60°C.

35

0.1 gram of the modified polymer was contacted for 2 hours with 20 ml of a 50 ppm chromium(VI) solution at a pH value of 2.0. The treated polyurethane sorbed 62% of

- 19 -

chromium(VI), whereas the untreated polyurethane only sorbed 6% of chromium(VI) under the same conditions.

0.1 gram of the modified polymer was contacted for 2 hours with 20 ml of a 50 ppm palladium(II) solution at a pH value of 2.0. The treated polyurethane sorbed 33% of palladium(II), whereas the untreated polyurethane only sorbed 15% of palladium(II) under the same conditions.

0.1 gram of the modified polymer was contacted for 2 hours with 20 ml of a 50 ppm platinum(II) solution at a pH value of 2.0. The treated polyurethane sorbed 73% of platinum(II), whereas the untreated polyurethane sorbed 31% of platinum(II) under the same conditions.

EXAMPLE 3B

THIOAMIDATION

1 gram of the copolymer-containing polyurethane foam was swollen in 70 ml of 1,2-dichloroethane together with benzyl trimethylammonium chloride as a catalyst and treated with 6 grams of sodium sulphide dissolved in 20 ml of water. Sufficient 0.5M sulphuric acid was slowly added over a period of two hours to the reaction mixture to maintain a slightly acidic condition. The polyurethane was then washed in water until neutral and vacuum dried at 60°C.

Prior to treatment the polyurethane failed to remove copper, zinc, and cobalt from solution; however, when the treated polyurethane was contacted with 20 ml of a solution containing 50 ppm copper(II) plus 50 ppm of zinc(II) plus 50 ppm of cobalt(II) for 2 hours 15% of the copper(II), 6% of the zinc(II) and 8% of the cobalt(II) were removed from the mixed aqueous solution at a pH of 5.0.

- 20 -

EXAMPLE 3CAMIDOXIMATION

5 (a) 1 gram of the copolymer-containing polyurethane foam was treated with 100 ml of a 3% aqueous solution of hydroxylamine at 80°C for 24 hours.

10 (b) Alternatively, 1 gram of the copolymer-containing polyurethane foam was treated with 2 grams of hydroxylamine plus 10 ml of pyridine in 70 ml of ethanol at 70°C for 8 hours.

15 (c) In a further alternative reaction, 1 gram of copolymer-containing polyurethane foam was reacted at 80°C for 4 hours with 20 ml of a 6% hydroxylamine solution in 60 ml of toluene with benzyl trimethylammonium chloride as a catalyst.

20 (d) A further alternative reaction, 1 gram of copolymer-containing polyurethane foam was reacted at 80°C for 24 hours with 80 ml of a 3% methanolic hydroxylamine solution in a pressure vessel.

25 Each of the foams described above was washed with water, then soaked for 30 minutes in 1M hydrochloric acid, then further washed with water until neutral and vacuum dried at 60°C.

30 0.1 gram of each of the above modified polymers was contacted for 2 hours with 20 ml of a 50 ppm chromium(VI) solution at a pH value of 2.0. The treated polyurethane in (a) sorbed 16% of chromium (VI), 15% of chromium(VI) for (b), 19% of chromium(VI) for (c), and 85% of
35 chromium(VI) for (d) whereas the untreated polyurethane only sorbed 6% of chromium(VI) under the same conditions.

- 21 -

EXAMPLE 3DPHOSPHORYLATION

- 5 1 g of a copolymer-containing polyurethane foam was
reacted for 4 hours at 20°C in 80 ml of 1,2
dichloroethane with 1 g of phosphorus trichloride in the
presence of 1 g of aluminium trichloride as a catalyst.
The resultant polymer was washed in 95% ethanol, 50%
10 aqueous ethanol, distilled water, 1 N NaOH solution,
distilled water, 1N NaCl solution and finally with
distilled water until free of unreacted reagents. The
polymer was then vacuum dried at 60°C.
- 15 0.1 gram of the above foam removed 17% of mercuric
chloride from an aqueous solution. 0.1 gram of the above
foam completely removed 100 ppm of gold cyanide from
aqueous solution.
- 20 Alternatively, 1 gram of the copolymer-containing
polyurethane foam was placed in 70 ml of toluene then
reacted at room temperature for four hours with 2.5 ml of
phosphorus oxychloride in 10 ml of pyridine. The foam
was then washed in water, 1M hydrochloric acid, and again
25 in water until neutral, then vacuum dried at 60°C.
- 0.1 gram of the treated polymer was contacted with
20 ml of a solution containing 50 ppm copper(II) plus
50 ppm of zinc(II) plus 50 ppm of cobalt(II) for 2 hours.
30 The treated polymer removed 44% of the copper(II), 24% of
the zinc(II) and 19% of the cobalt(II) from an aqueous
solution at a pH of 5.0, whereas the untreated polymer
did not indicate any observable removal of these metal
ions under the same conditions.

35

- 22 -

EXAMPLE 3ECHLOROMETHYLATION

5 1 gram of the copolymer-containing polyurethane foam
was swollen in 80 ml of chloroform then reacted at room
temperature for 2 hours with 5 grams of octyl
chloromethyl ether in 20 ml of chloroform together with
stannic tetrachloride as a catalyst. (Octyl chloromethyl
10 ether solution was produced by reacting 13 grams of
octanol with 3 grams of paraformaldehyde in 100 ml of
chloroform through which dry hydrochloric gas was
bubbled. The reaction was conducted for 2 hours.)

15 (a) Amination

The chloromethylated polymer foam was then aminated
by reacting 1 gram of it with 0.1 gram of
diethylenetriamine in 80 ml of toluene at 75°C for four
20 hours.

0.1 gram of the modified polymer was contacted for 2
hours with 20 ml of a 50 ppm chromium(VI) solution at a
pH value of 2.0. The treated polymer sorbed 57% of
25 chromium(VI), whereas the untreated polymer only sorbed
6% of chromium(VI) under the same conditions.

0.1 gram of the treated polymer was contacted with
20 ml of a solution containing 50 ppm copper(II) plus
30 50 ppm of zinc(II) plus 50 ppm of cobalt(II) for 2 hours.
The treated polymer selectively removed 18% of the
copper(II) from the mixed aqueous solution at a pH of
5.0, whereas the untreated polymer foam did not indicate
any observable removal of metal ions under the same
35 conditions.

- 23 -

(b) Phosphorylation

1 gram of the aminated polymer described in (a) above was then placed in 80 ml of toluene and further
5 reacted at room temperature for 4 hours with 2.5 grams of phosphorus oxychloride in 10 ml of pyridine.

The polymer was washed with water, then 1 M hydrochloric acid and again with water until neutral.
10 The polymer was then vacuum dried at 60°C.

The chloromethylated polymer which had been aminated, and then further phosphorylated was evaluated for the removal of copper, zinc and cobalt from aqueous
15 solution at a pH value of 5.0 as follows:

0.1 gram of the treated polymer was contacted with 20 ml of a solution containing 50 ppm copper(II) plus 50 ppm of zinc(II) plus 50 ppm of cobalt(II) for 2 hours. The treated polymer removed 57% of the copper(II), 32% of
20 the zinc(II) and 23% of the cobalt(II) from an aqueous solution, whereas the untreated polymer did not indicate any observable removal of metal ions under the same conditions.

25 It should be noted that this method of phosphorylation gave an approximate increase in metal ion removal of 50% over the phosphorylated copolymer-containing polyurethane reported in Example 3D above.

30 Phosphorylation of the aminated site was confirmed by a substantial reduction in sorption of chromium(VI) from solution. 0.1 gram of this phosphorylated polymer was contacted for 2 hours with 20 ml of a 50 ppm chromium(VI) solution at a pH value of 2.0. The
35 phosphorylated polymer sorbed 11% of chromium(VI), whereas the aminated polymer as described in (a) above sorbed 57% of chromium(VI) under the same conditions.

- 24 -

(c) Thioureaation/isothiuronium resins

1 gram of the chloromethylated polymer was added to a solution of thiourea in water at 85°C for 6 hours.

- 5 After the reaction reached completion the resin was rinsed in distilled water, 1N HCl, distilled water, then in acetone and dried.

- The resulting resin was used to recover gold and
10 platinum group metals from aqueous solutions.

EXAMPLE 4

EXAMPLES BASED ON INCORPORATION OF INTERPENETRATING
15 POLYMER AFTER PRODUCTION OF POLYURETHANE

- Polyurethane foams were produced from a blend of a 5000 MW polyol containing a high content of poly(ethylene oxide) units with a 4800 MW poly(ethylene oxide) capped
20 polyol under different catalyst regimes. The polyols were both based on glycerine, one containing approximately 75% of poly(ethylene oxide) units and the other, 15% of poly(ethylene oxide) units as a capping (ethylene oxide content was determined by NMR), thus many
25 of the terminal units consist of primary hydroxyls thus providing the polyol with self-catalysing properties. To the polyol was added in appropriate quantities, water, silicone surfactant, and stannous octoate as a catalyst. The mixture was then reacted with the required quantity
30 of toluene diisocyanate to produce a foam.

- This polyurethane had previously been observed to have a significantly improved chemical and solvent resistance and was used in all of the following examples.
35 Interpenetration was conducted by soaking it in a suitable monomer or blend of monomers which were then polymerised to produce an interpenetrated polyurethane.

- 25 -

The following examples are typical of interpenetrated systems which can be produced by this method. Once cured, the interpenetrated polyurethanes were then chemically modified using the techniques previously described (or as given hereunder).

EXAMPLE 4A

METHACRYLONITRILE (MAN)-DIVINYLBENZENE (DVB)

10

An appropriate quantity, typically 3 grams, of the polyurethane previously described was soaked for one hour in the following mixture:

20 grams of MAN plus 6 grams of DVB plus 0.02 grams of potassium persulphate as a polymerisation initiator.

After soaking the polyurethane in this mixture it was transferred to an aqueous solution containing a suitable surfactant plus isooctylmercaptopropionate as a catalyst. Curing was conducted at 90°C for 15 hours. The interpenetrated polyurethane was washed with water and oven dried. This material is now a precursor for further chemical modification.

25 (a) Amination

1 gram of the above interpenetrated polyurethane foam was reacted for six hours at 90°C in 80 ml of toluene with 0.1 g of diethylenetriamine in the presence of rubeanic acid as a catalyst. The foam was washed in water until neutral, then vacuum dried at 60°C.

0.1 gram of the modified polymer was contacted for 2 hours with 20 ml of a 50 ppm chromium(VI) solution at a pH value of 2.0. The treated polymer sorbed 47% of chromium(VI), whereas the untreated material only sorbed 25% of chromium(VI) under the same conditions.

- 26 -

EXAMPLE 4BACRYLIC ACID (AA)-ACRYLAMIDE (AM)

5 (a) Three grams of the polyurethane previously described was soaked for one hour in the following mixture:

20 grams of AA plus 10 grams of AM plus 0.02 grams of potassium persulphate as a polymerisation initiator.

10

After soaking the polyurethane in this mixture, the polymer was transferred to an aqueous solution containing isooctylmercaptopropionate as a catalyst. Curing was conducted at 90°C for 15 hours. The interpenetrated
15 polyurethane was washed in water and oven dried.

(b) Alternatively, the polyurethane previously described was soaked for one hour in the following mixture:

20

5 grams of AA plus 10 grams of AM dissolved in 15 grams of cyclohexane and containing 0.02 grams of potassium persulphate as a polymerisation initiator.

After soaking the polyurethane in this mixture, the
25 polymer was transferred to an aqueous solution containing isooctylmercaptopropionate as a catalyst. Curing was conducted at 90°C for 15 hours. The interpenetrated polyurethane was washed in water and oven dried.

30 0.1 gram of each of the treated polyurethanes was separately contacted with 20 ml of a solution containing 50 ppm copper(II) plus 50 ppm of zinc(II) plus 50 ppm of cobalt(II) for 2 hours. The treated polyurethanes selectively removed 26% of copper(II) for (a) and 32% of
35 copper(II) for (b), from the mixed aqueous solution, whereas the untreated foam did not indicate any observable removal of metal ions under the same

- 27 -

conditions.

It was observed that the change in the ratio of AA to AM also gave a substantial change in the uptake of chromium(VI) at a pH value of 2.0.

0.1 gram of the treated polyurethane was contacted for 2 hours with 20 ml of a 50 ppm chromium(VI) solution at a pH value of 2.0. The treated polyurethane sorbed 34% of chromium(VI), whereas the untreated polyurethane sorbed 25% of chromium(VI) under the same conditions.

EXAMPLE 4C

POLYSTYRENE-DIVINYL BENZENE

Three grams of the polyurethane previously described was soaked for one hour in the following mixture:

30 grams of styrene monomer plus 5 grams of divinyl benzene (DVB) plus 0.02 grams of potassium persulphate as a polymerisation initiator.

After soaking the polyurethane in this mixture, the polymer was transferred to an aqueous solution containing a suitable surfactant plus isooctylmercaptopropionate as a catalyst. Curing was conducted at 80°C for 15 hours. The interpenetrated polyurethane was washed in water and oven dried.

CHLOROMETHYLATION:

(a) Chloromethylation of 1 gram of a polyurethane containing polymerised p-methylstyrene was accomplished using aqueous sodium hypochlorite. Benzyltriethylammonium chloride was used as the catalyst. The reaction was conducted at room temperature for 16 hours in 80 ml of 1,2-dichloroethane under an argon atmosphere.

- 28 -

(b) 1 gram of the polystyrene divinylbenzene interpenetrated polyurethane foam described above was swollen in 70 ml of chloroform and reacted at room temperature for 2 hours with 5 grams of octyl
5 chloromethyl ether solution together with stannic tetrachloride. (Octyl chloromethyl ether was produced by reacting 13 grams of octanol plus 3 grams of paraformaldehyde in 100 ml of chloroform through which dry hydrochloric gas was bubbled. The reaction was
10 conducted for 2 hours.)

AMINATION

The chloromethylated polymer as given in (b) above
15 was then aminated by reacting 1 gram of it at 75°C for four hours with 0.1 gram of diethylenetriamine in 80 ml of toluene. The polymer was washed with water until neutral and vacuum dried at 60°C.

20 0.1 gram of this polymer was contacted for 2 hours with 20 ml of a 50 ppm chromium(VI) solution at a pH value of 2.0. The treated polymer sorbed 40% of chromium(VI), whereas the untreated polymer sorbed 25% of chromium(VI) under the same conditions.

25

PHOSPHORYLATION

The chloromethylated polymer as given in (b) above, was phosphorylated as follows:

30 1 gram of the chloromethylated polymer was placed in 80 ml of 1,2 dichloromethane together with 1.6 grams of phosphorus trichloride and aluminium chloride as a catalyst. The phosphorylated polymer was washed in water until neutral and vacuum dried at 60°C.

35

0.1 gram of the treated polymer was contacted with 20 ml of a solution containing 50 ppm copper(II) plus

- 29 -

50 ppm of zinc(II) plus 50 ppm of cobalt(II) for 2 hours. The treated polymer selectively removed 12% of copper(II) from the mixed aqueous solution, whereas the untreated foam did not indicate any observable removal of metal ions under the same conditions.

EXAMPLE 4D

POLYSTYRENE-METHACRYLONITRILE

10

Three grams of the polyurethane previously described was soaked for one hour in the following mixture:

30 grams of styrene monomer plus 20 grams of methacrylonitrile (MAN) plus 0.02 grams of potassium persulphate as a polymerisation initiator.

15

After soaking the polyurethane in this mixture, the polymer was transferred to an aqueous solution containing a suitable surfactant plus isooctylmercaptopropionate as a catalyst. Curing was conducted at 80°C for 15 hours. The interpenetrated polyurethane was washed in water and oven dried. Changes in the physical properties of the final cured polymer indicated that the interpenetration had been successfully conducted.

25

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications which fall within its spirit and scope.

30

- 30 -

CLAIMS:-

1. An ion exchange resin comprising an ion exchange material dispersed or distributed throughout a
5 polyurethane matrix.
2. An ion exchange resin according to claim 1 wherein the ion exchange material is a second polymer which has been chemically modified after dispersion or distribution
10 throughout the polyurethane matrix.
3. An ion exchange resin according to claim 2 wherein the polyurethane matrix and said second polymer form an interpenetrating polymer system, said second polymer
15 being an interpenetrated polymer.
4. An ion exchange resin according to claim 2 wherein the dispersed or distributed phase polymer is a polymer formed from monomers of styrene, acrylonitrile, vinyl
20 chloride, vinylidene chloride, divinyl benzene, butadiene, epichlorohydrin, caprolactone, thiodiglycol, thiodianiline, diallylamine, methylacrylonitrile, hydrazides, dicyclopentadiene, vinyl butyral, succinic anhydride, allyl halides, allyl malonic acid, acryloyl
25 chloride, polyacetal, vinyl alcohol, aminosalicylic acid, dimethylolpropionic acid, α -methyl styrene, p-methyl styrene, acrylates such as methylmethacrylate, acrylamide, methylacrylamide, acrylic acid, hydroxyethyl acrylate, hydroxypropyl acrylate, glycidyl methacrylate,
30 ethylene dimethacrylate, methylacrylic acid, hydroxyethyl methacrylate, ethylene glycol dimethacrylate, ethyl acrylate, acrylimido salicylic acid, acrylimido diacetic acid, acrylimido malonic acid, acrylimido phthalic acid, acrylimido glycolic acid, or combinations and/or chemical
35 modifications thereof.
5. An ion exchange resin according to claim 4 wherein

the chemically modified monomers are selected from hydroxy styrenes, vinylbenzyl chloride, hydroxyethyl styrene, α -methyl styrene, p-methyl styrene, dihydroxyethyl styrene, styrene sulphonic acid, acetoxystyrene.

6. An ion exchange resin according to claim 2 wherein the dispersed or distributed phase polymer is selected from polystyrene, styrene-divinyl benzene, styrene-acrylonitrile, styrene-acrylonitrile-methylmethacrylate, acrylonitrile-methylmethacrylate, polyacrylonitrile, polyacrylates, acrylic or methacrylic esters, acrylonitrile-unsaturated dicarboxylic acid-styrene, vinylidene chloride-acrylonitrile, epoxy(glycidyl methacrylate)-acrylonitrile, poly p-methylstyrene, polyureas, aniline phenolformaldehyde, phenol-formaldehyde, styrene-butadiene, styrene-acrylonitrile-butadiene, acrylonitrile-polyethylene glycol, polyamides, polyacrylamides, polyimidazoles, allylglycidyl ether adducts of diamines, ethylene and propylene carbonate adducts of diamines, polybutadiene acrylates, polydiallylamine, epoxy adducts, polycaprolactone, caprolactone-acrylates, polydicyclopentadiene, styrenemethacrylonitrile, methacrylonitrile-divinylbenzene, polyvinyl chloride, glycidyl methacrylate-ethylene dimethacrylate, acrylonitrile-methylacrylic acid, polyvinyl alcohol-acrylonitrile, methyl methacrylate-hydroxyethyl acrylate, hydroxyethyl methacrylate-oligo(ethylene glycol)dimethacrylate, hydroxystyrenemethylmethacrylate, polyethyl acrylate-polystyrene, crosslinked butadiene, polystyrene-polyethyleneimine, polystyrene-arsenazo, epoxy-polystyrene, epoxy-diazacrown ethers, polyacetal, cresol sulphonic acid-phenol-formaldehyde, anthraquinone-formaldehyde, acryloyl chloride-iminodiacetic acid, acryloyl chloride-aminosalicylic acid, acryloyl chloride-methylnitrophenol-triethylamine, methyl nitrophenol-acetic

- 32 -

anhydride-acrylic acid, hydroxy acetophenone-substituted benzoic acid-formaldehyde, or combinations thereof.

7. A ion exchange resin according to claim 2 wherein
5 said polyurethane matrix has been formed from an isocyanate or hydroxy terminated prepolymer.

8. An ion exchange resin according to claim 2 wherein
said polyurethane matrix is also chemically modified.

10

9. An ion exchange resin according to claim 1 wherein
active sites are incorporated into the polyurethane
matrix.

15

10. An ion exchange resin according to claim 2 wherein
the dispersed or distributed phase polymer has been
chemically modified by one or more of chloromethylation,
sulphonation, carboxylation, amination, phosphorylation,
thioureaation, diazotization, amidoximation, or oximation
20 in one or more steps.

25

11. A resin according to claim 3 wherein melamine,
melamine formaldehyde or solvent extractants containing
phosphorus, or nitrogen or sulphur or any combination of
these have been incorporated into the interpenetrated
polymer.

30

12. A method of producing an ion exchange resin
comprising:

providing a polyurethane matrix and subsequently
having a second polymer dispersed or distributed therein
by interpenetrating the polyurethane polymer with
polymerisable monomers and subsequently curing them; and
chemically modifying said second polymer to obtain
35 desired ion exchange properties.

- 33 -

13. A method according to claim 12 wherein said polyurethane matrix is also chemically modified.

14. A method of producing an ion exchange resin

5 comprising:

providing a polyurethane interpenetrating polymer system which comprises a polyurethane polymer having a second polymer dispersed or distributed therein; and

10 chemically modifying said second polymer to obtain the desired ion exchange properties.

15 15. A method of producing an ion exchange resin comprising:

providing a polyol having a second polymer dispersed therein;

reacting said polyol with a diisocyanate or a blend of diisocyanates to produce a polyurethane having said second polymer dispersed therein; and

20 chemically modifying said second polymer to obtain desired ion exchange properties.

16. A method of producing an ion exchange resin comprising:

25 providing a polyurethane containing a resin having ion exchange properties dispersed or distributed therein; and

chemically modifying said resin to modify the ion exchange properties.

30 17. Use of an ion exchange resin according to claim 1 in removing soluble electrolytes in waste water treatment processes or hydrometallurgical processes.

18. A method for removing soluble electrolytes from a solvent comprising:

35 contacting the solvent with an ion exchange resin according to claim 1; and

- 34 -

recovering the electrolytes from the ion exchange resin.

19. A method according to claim 18 wherein the ion
5 exchange resin is mixed with the solvent and subsequently
recovered from the solvent prior to recovering the
electrolytes from the resin.

20. A method according to claim 18 wherein the solvent
10 is passed through a bed containing the ion exchange
resin.

21. A method for recovering soluble electrolytes in a
hydrometallurgical process including:
15 contacting an ion exchange resin according to
claim 1 with a solution containing a suspension of ore
solids; and
 recovering the ion exchange resin.

20 22. A process according to claim 21 wherein the soluble
electrolytes are selected from ions of gold, zinc,
copper, chromium, palladium, platinum, silver, cobalt,
mercury, arsenic, molybdenum and mixtures thereof.

25 23. A process according to claim 21 wherein the ion
exchange resin is in the form of granules.

24. A process according to claim 21 wherein the ion
exchange resin is recovered by screening.

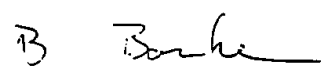
30 25. A process according to claim 21 wherein the ion
exchange resin contains a magnetic material and the ion
exchange resin is recovered by magnetic separation.

35 26. A method of recovering soluble electrolytes from
waste water comprising:
 contacting an ion exchange resin according to

- 35 -

claim 1 with said waste water; and
recovering the electrolytes from the ion exchange
resin.

- 5 27. A method according to claim 26 wherein the waste
water is an industrial effluent or sewage effluent.
28. Use of an ion exchange resin according to claim 1 to
treat effluent streams to recover desired metal ions
10 contained therein.
29. Use of an ion exchange resin according to claim 1 to
remove toxic metals from a discharge of an effluent.
- 15 30. Use according to claim 29 wherein the toxic metal
and/or the effluent is subsequently recycled.
31. Use of an ion exchange resin according to claim 1 in
a hydrometallurgical process to extract or recover metal
20 ions from a clarified lixiviant, a process solution
partly clarified by removal of larger ore solids, or ore
solids in the form of a pulp.

A. CLASSIFICATION OF SUBJECT MATTER Int. Cl. ⁵ B01J39/18, 41/12, 43/00//C02F 1/42 According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC:B01J 39/18, 41/12, 43/00 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AU:IPC as above Electronic data base consulted during the international search (name of data base, and where practicable, search terms used)				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.		
X, Y	GB,A,944903 (ROHM & HAAS COMPANY) 18 December 1963 (18.12.63)	(1-24,26-31)		
X, Y	US,A,3094494 (HOPKINS et al) 18 June 1963 (18.06.63)	(1-24,26-31)		
X	DE,E,3019615 (Leningradskij institut tekstil'nojilegkojpromyslennostilmeni S.M.Korova) 3 December 1981 (03.12.81)	(1)		
X	Patent Abstracts of Japan, C-58, page 49, JP,A,56-33044 (TOYO GOMU KOGYO K.K.) 3 April 1981 (03.04.81)	(1)		
<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="display: flex; align-items: center;"> <input type="checkbox"/> Further documents are listed in the continuation of Box C. </div> <div style="display: flex; align-items: center;"> <input checked="" type="checkbox"/> See patent family annex. </div> </div>				
<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; vertical-align: top;"> <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </td> <td style="width: 50%; vertical-align: top;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p> </td> </tr> </table>			<p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>
<p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>			
Date of the actual completion of the international search 10 September 1993 (10.09.93)		Date of mailing of the international search report 22 SEP 1993 (22.09.93)		
Name and mailing address of the ISA/AU AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No. 06 2853929		Authorized officer <div style="text-align: center; margin-top: 20px;">  </div> B. Bourke Telephone No. (06) 2832138		

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No.
X	Derwent Abstract Accession No. 91-110158/16, Class A91, DD,A,284475 (AKAD WISS DDR MOLEK) 14 November 1990 (14.11.90)	(1)
X	Derwent Abstract Accession No. 91-110100/16, Class A91, DD,A,284416 (ADAD WISSENSCHAFT DDR (MOLE-) 14 November 1990 (14.11.90)	(1)
X	Derwent Abstract Accession No. 91-110156/16 Class A91, DD,A,284473 (AKAD WISS DDR MOLEK) 14 November 1990 (14.11.90)	(1)
X	Derwent Abstract Accession No. 91-110157/16 Class A91,DD,A,284474 (AKAD WISS MOLEKUL) 14 November 1990 (14.11.90)	(1)

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member
DE	3019615	
JP	56033044	
DD	284475	
DD	284416	
DD	284473	
DD	260408	
		END OF ANNEX